

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C22C 38/44, 38/50	A1	(11) International Publication Number: WO 99/07910 (43) International Publication Date: 18 February 1999 (18.02.99)
(21) International Application Number: PCT/US98/15839 (22) International Filing Date: 30 July 1998 (30.07.98) (30) Priority Data: 08/907,305 6 August 1997 (06.08.97) US (71) Applicant: CRS HOLDINGS, INC. [US/US]; 209F Baynard Building, 3411 Silverside Road, Wilmington, DE 19810 (US). (72) Inventor: MARTIN, James, W.; 11 Marie Drive, Sinking Spring, PA 19608 (US). (74) Agents: BRUSTEIN, Mitchell, R. et al.; Dann, Dorfman, Herrell and Skillman, P.C., Suite 720, 1601 Market Street, Philadelphia, PA 19103-2307 (US).		(81) Designated States: BR, CA, IL, JP, KR, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HIGH-STRENGTH, NOTCH-DUCTILE PRECIPITATION-HARDENING STAINLESS STEEL ALLOY (57) Abstract A precipitation hardenable, martensitic stainless steel alloy is disclosed consisting essentially of, in weight percent, about: C 0.03 max, Mn 1.0 max, Si 0.75 max, P 0.040 max, S 0.020 max, Cr 10 - 13, Ni 10.5 - 11.6, Ti 1.5 - 1.8, Mo 0.25 - 1.5, Cu 0.95 max, Al 0.25 max, Nb 0.3 max, B 0.010 max, N 0.030 max, Ce 0.001 - 0.025, the balance essentially iron. The disclosed alloy provides a unique combination of stress-corrosion cracking resistance, strength, and notch toughness even when used to form large cross-section pieces. A method of making such an alloy includes adding cerium during the melting process in a amount sufficient to yield an effective amount of cerium in the alloy product.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

High-Strength, Notch-Ductile Precipitation-Hardening
Stainless Steel Alloy

Field of the Invention

The present invention relates to precipitation
hardenable, martensitic stainless steel alloys and in
10 particular to a Cr-Ni-Ti-Mo martensitic stainless
steel alloy, and an article made therefrom, having a
unique combination of stress-corrosion cracking
resistance, strength, and notch toughness.

15 Background of the Invention

Many industrial applications, including the
aircraft industry, require the use of parts
manufactured from high strength alloys. One approach
to the production of such high strength alloys has
20 been to develop precipitation hardening alloys. A
precipitation hardening alloy is an alloy wherein a
precipitate is formed within the ductile matrix of the
alloy. The precipitate particles inhibit dislocations
within the ductile matrix thereby strengthening the
25 alloy.

One of the known age hardening stainless steel
alloys seeks to provide high strength by the addition
of titanium and columbium and by controlling chromium,
nickel, and copper to ensure a martensitic structure.
30 To provide optimum toughness, this alloy is annealed
at a relatively low temperature. Such a low annealing

temperature is required to form an Fe-Ti-Nb rich Laves phase prior to aging. Such action prevents the excessive formation of hardening precipitates and provides greater availability of nickel for austenite reversion. However, at the low annealing temperatures used for this alloy, the microstructure of the alloy does not fully recrystallize. These conditions do not promote effective use of hardening element additions and produce a material whose strength and toughness are highly sensitive to processing.

In another known precipitation hardenable stainless steel the elements chromium, nickel, aluminum, carbon, and molybdenum are critically balanced in the alloy. In addition, manganese, silicon, phosphorus, sulfur, and nitrogen are maintained at low levels in order not to detract from the desired combination of properties provided by the alloy.

While the known precipitation hardenable, stainless steels have hitherto provided acceptable properties, a need has arisen for an alloy that provides better strength together with at least the same level of notch toughness and corrosion resistance provided by the known precipitation hardenable, stainless steels. An alloy having higher strength while maintaining the same level of notch toughness and corrosion resistance, particularly resistance to stress corrosion cracking, would be particularly useful in the aircraft industry because structural members fabricated from such alloys could be lighter in weight than the same parts manufactured from currently available alloys. A reduction in the weight of such structural members is desirable since it results in improved fuel efficiency.

Given the foregoing, it would be highly desirable to have an alloy which provides an improved combination of stress-corrosion resistance, strength, and notch toughness while being easily and reliably processed.

Summary of the Invention

The shortcomings associated with the known precipitation hardenable, martensitic stainless steel alloys are solved to a large degree by the alloy in accordance with the present invention. The alloy according to the present invention is a precipitation hardening Cr-Ni-Ti-Mo martensitic stainless steel alloy that provides a unique combination of stress-corrosion cracking resistance, strength, and notch toughness.

The broad, intermediate, and preferred compositional ranges of the precipitation hardening, martensitic stainless steel of the present invention are as follows, in weight percent:

		<u>Broad</u>	<u>Intermediate</u>	<u>Preferred</u>
25	C	0.03 max	0.02 max	0.015 max
	Mn	1.0 max	0.25 max	0.10 max
	Si	0.75 max	0.25 max	0.10 max
	P	0.040 max	0.015 max	0.010 max
	S	0.020 max	0.010 max	0.005 max
	Cr	10 - 13	10.5 - 12.5	11.0 - 12.0
30	Ni	10.5 - 11.6	10.75 - 11.25	10.85 - 11.25
	Ti	1.5 - 1.8	1.5 - 1.7	1.5 - 1.7
	Mo	0.25 - 1.5	0.75 - 1.25	0.9 - 1.1
	Cu	0.95 max	0.50 max	0.25 max
	Al	0.25 max	0.050 max	0.025 max
35	Nb	0.3 max	0.050 max	0.025 max
	B	0.010 max	0.001 - 0.005	0.0015 - 0.0035
	N	0.030 max	0.015 max	0.010 max
	Ce	up to 0.025	0.001 - 0.015	0.002 - 0.010

40

The balance of the alloy is essentially iron except for the usual impurities found in commercial grades of such steels and minor amounts of additional elements which may vary from a few thousandths of a

percent up to larger amounts that do not objectionably detract from the desired combination of properties provided by this alloy.

The foregoing tabulation is provided as a
5 convenient summary and is not intended thereby to restrict the lower and upper values of the ranges of the individual elements of the alloy of this invention for use in combination with each other, or to restrict
10 the ranges of the elements for use solely in combination with each other. Thus, one or more of the element ranges of the broad composition can be used with one or more of the other ranges for the remaining elements in the preferred composition. In addition, a
15 minimum or maximum for an element of one preferred embodiment can be used with the maximum or minimum for that element from another preferred embodiment. Throughout this application, unless otherwise indicated, percent (%) means percent by weight.

20 Detailed Description

In the alloy according to the present invention, the unique combination of strength, notch toughness, and stress-corrosion cracking resistance is achieved by balancing the elements chromium, nickel, titanium,
25 and molybdenum. At least about 10%, better yet at least about 10.5%, and preferably at least about 11.0% chromium is present in the alloy to provide corrosion resistance commensurate with that of a conventional stainless steel under oxidizing conditions. At least
30 about 10.5%, better yet at least about 10.75%, and preferably at least about 10.85% nickel is present in the alloy because it benefits the notch toughness of the alloy. At least about 1.5% titanium is present in the alloy to benefit the strength of the alloy through
35 the precipitation of a nickel-titanium-rich phase

during aging. At least about 0.25%, better yet at least about 0.75%, and preferably at least about 0.9% molybdenum is also present in the alloy because it contributes to the alloy's notch toughness.

- 5 Molybdenum also benefits the alloy's corrosion resistance in reducing media and in environments which promote pitting attack and stress-corrosion cracking.

- When chromium, nickel, titanium, and/or molybdenum are not properly balanced, the alloy's ability to transform fully to a martensitic structure using conventional processing techniques is inhibited. Furthermore, the alloy's ability to remain substantially fully martensitic when solution treated and age-hardened is impaired. Under such conditions
- 10 the strength provided by the alloy is significantly reduced. Therefore, chromium, nickel, titanium, and molybdenum present in this alloy are restricted. More particularly, chromium is limited to not more than about 13%, better yet to not more than about 12.5%, and preferably to not more than about 12.0% and nickel
- 20 is limited to not more than about 11.6% and preferably to not more than about 11.25%. Titanium is restricted to not more than about 1.8% and preferably to not more than about 1.7% and molybdenum is restricted to not more than about 1.5%, better yet to not more than about 1.25%, and preferably to not more than about 1.1%.

- Sulfur and phosphorus tend to segregate to the grain boundaries of this alloy. Such segregation
- 30 reduces grain boundary adhesion which adversely affects the fracture toughness, notch toughness, and notch tensile strength of the alloy. A product form of this alloy having a large cross-section, i.e., $>0.7 \text{ in}^2$ ($>4 \text{ cm}^2$), does not undergo sufficient thermomechanical processing to homogenize the alloy
- 35

and neutralize the adverse effect of sulfur and phosphorus concentrating in the grain boundaries. For large section size products, a small addition of cerium is preferably made to the alloy to benefit the fracture toughness, notch toughness, and notch tensile strength of the alloy by combining with sulfur and phosphorus to facilitate their removal from the alloy. For the sulfur and phosphorus to be adequately scavenged from the alloy, the ratio of the amount of cerium added to the amount of sulfur present in the alloy is at least about 1:1, better yet at least about 2:1, and preferably at least about 3:1. Only a trace amount (i.e., <0.001%) of cerium need be retained in the alloy for the benefit of the cerium addition to be realized. However, to insure that enough cerium has been added and to prevent too much sulfur and phosphorus from being retained in the final product, at least about 0.001% and better yet at least about 0.002% cerium is preferably present in the alloy. Too much cerium has a deleterious affect on the hot workability of the alloy and on its fracture toughness. Therefore, cerium is restricted to not more than about 0.025%, better yet to not more than about 0.015%, and preferably to not more than about 0.010%. Alternatively, the cerium-to-sulfur ratio of the alloy is not more than about 15:1, better yet not more than about 12:1, and preferably not more than about 10:1. Magnesium, yttrium, or other rare earth metals such as lanthanum can also be present in the alloy in place of some or all of the cerium.

Additional elements such as boron, aluminum, niobium, manganese, and silicon may be present in controlled amounts to benefit other desirable properties provided by this alloy. More specifically, up to about 0.010% boron, better yet up to about

0.005% boron, and preferably up to about 0.0035% boron can be present in the alloy to benefit the hot workability of the alloy. In order to provide the desired effect, at least about 0.001% and preferably
5 at least about 0.0015% boron is present in the alloy.

Aluminum and/or niobium can be present in the alloy to benefit the yield and ultimate tensile strengths. More particularly, up to about 0.25%, better yet up to about 0.10%, still better up to about
10 0.050%, and preferably up to about 0.025% aluminum can be present in the alloy. Also, up to about 0.3%, better yet up to about 0.10%, still better up to about 0.050%, and preferably up to about 0.025% niobium can be present in the alloy. Although higher yield and
15 ultimate tensile strengths are obtainable when aluminum and/or niobium are present in this alloy, the increased strength is developed at the expense of notch toughness. Therefore, when optimum notch toughness is desired, aluminum and niobium are
20 restricted to the usual residual levels.

Up to about 1.0%, better yet up to about 0.5%, still better up to about 0.25%, and preferably up to about 0.10% manganese and/or up to about 0.75%, better yet up to about 0.5%, still better up to about 0.25%,
25 and preferably up to about 0.10% silicon can be present in the alloy as residuals from scrap sources or deoxidizing additions. Such additions are beneficial when the alloy is not vacuum melted. Manganese and/or silicon are preferably kept at low
30 levels because of their deleterious effects on toughness, corrosion resistance, and the austenite-martensite phase balance in the matrix material.

The balance of the alloy is essentially iron apart from the usual impurities found in commercial grades
35 of alloys intended for similar service or use. The

levels of such elements are controlled so as not to adversely affect the desired properties.

In particular, too much carbon and/or nitrogen impair the corrosion resistance and deleteriously affect the toughness provided by this alloy. Accordingly, not more than about 0.03%, better yet not more than about 0.02%, and preferably not more than about 0.015% carbon is present in the alloy. Also, not more than about 0.030%, better yet not more than about 0.015%, not more than about 0.010% nitrogen is present in the alloy. When carbon and/or nitrogen are present in larger amounts, the carbon and/or nitrogen bonds with titanium to form titanium-rich non-metallic inclusions. That reaction inhibits the formation of the nickel-titanium-rich phase which is a primary factor in the high strength provided by this alloy.

Phosphorus is maintained at a low level because of its deleterious effect on toughness and corrosion resistance. Accordingly, not more than about 0.040%, better yet not more than about 0.015%, and preferably not more than about 0.010% phosphorus is present in the alloy.

Not more than about 0.020%, better yet not more than about 0.010%, and preferably not more than about 0.005% sulfur is present in the alloy. Larger amounts of sulfur promote the formation of titanium-rich non-metallic inclusions which, like carbon and nitrogen, inhibit the desired strengthening effect of the titanium. Also, greater amounts of sulfur deleteriously affect the hot workability and corrosion resistance of this alloy and impair its toughness, particularly in a transverse direction.

Too much copper deleteriously affects the notch toughness, ductility, and strength of this alloy. Therefore, the alloy contains not more than about

0.95%, better yet not more than about 0.75%, still better not more than about 0.50%, and preferably not more than about 0.25% copper.

No special techniques are required in melting, casting, or working the alloy of the present invention. Vacuum induction melting (VIM) or vacuum induction melting followed by vacuum arc remelting (VAR) are the preferred methods of melting and refining, but other practices can be used. The preferred method of providing cerium in this alloy is through the addition of mischmetal during VIM. The mischmetal is added in an amount sufficient to yield the necessary amount of cerium, as discussed hereinabove, in the final as-cast ingot. In addition, this alloy can be made using powder metallurgy techniques, if desired. Further, although the alloy of the present invention can be hot or cold worked, cold working enhances the mechanical strength of the alloy.

The precipitation hardening alloy of the present invention is solution annealed to develop the desired combination of properties. The solution annealing temperature should be high enough to dissolve essentially all of the undesired precipitates into the alloy matrix material. However, if the solution annealing temperature is too high, it will impair the fracture toughness of the alloy by promoting excessive grain growth. Typically, the alloy of the present invention is solution annealed at 1700 °F - 1900 °F (927 °C - 1038 °C) for 1 hour and then quenched.

When desired, this alloy can also be subjected to a deep chill treatment after it is quenched, to further develop the high strength of the alloy. The deep chill treatment cools the alloy to a temperature sufficiently below the martensite finish temperature

to ensure the completion of the martensite transformation. Typically, a deep chill treatment consists of cooling the alloy to below about -100°F (-73°C) for about 1 hour. However, the need for a
5 deep chill treatment will be affected, at least in part, by the martensite finish temperature of the alloy. If the martensite finish temperature is sufficiently high, the transformation to a martensitic structure will proceed without the need for a deep
10 chill treatment. In addition, the need for a deep chill treatment may also depend on the size of the piece being manufactured. As the size of the piece increases, segregation in the alloy becomes more significant and the use of a deep chill treatment
15 becomes more beneficial. Further, the length of time that the piece is chilled may need to be increased for large pieces in order to complete the transformation to martensite. For example, it has been found that in a piece having a large cross-sectional area, a deep
20 chill treatment lasting about 8 hours is preferred for developing the high strength that is characteristic of this alloy.

The alloy of the present invention is age hardened in accordance with techniques used for the known
25 precipitation hardening, stainless steel alloys, as are known to those skilled in the art. For example, the alloys are aged at a temperature between about 900°F (482°C) and about 1150°F (621°C) for about 4 hours. The specific aging conditions used are
30 selected by considering that: (1) the ultimate tensile strength of the alloy decreases as the aging temperature increases; and (2) the time required to age harden the alloy to a desired strength level increases as the aging temperature decreases.

The alloy of the present invention can be formed into a variety of product shapes for a wide variety of uses and lends itself to the formation of billets, bars, rod, wire, strip, plate, or sheet using conventional practices. The alloy of the present invention is useful in a wide range of practical applications which require an alloy having a good combination of stress-corrosion cracking resistance, strength, and notch toughness. In particular, the alloy of the present invention can be used to produce structural members and fasteners for aircraft and the alloy is also well suited for use in medical or dental instruments.

15

Table 1

Ex./Ht. No.	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Ti	B	N	Nb	Al	Ce	Fe
1	0.003	0.09	0.02	0.006	0.003	11.54	11.13	1.00	0.05	1.61	0.0013	0.004	<0.01	---	---	Bal.
2	0.006	0.08	0.05	0.008	0.005	11.57	11.02	1.00	0.05	1.52	0.0019	0.004	<0.01	<0.01	---	Bal.
3	0.009	0.08	0.04	0.008	0.004	11.61	11.03	1.00	0.06	1.68	0.0021	0.005	<0.01	<0.01	---	Bal.
4	0.008	0.08	0.05	0.007	0.004	11.60	11.05	1.43	0.05	1.52	0.0020	0.005	<0.01	<0.01	---	Bal.
5	0.012	0.08	0.07	0.010	0.003	11.58	10.46	1.00	0.06	1.58	0.0024	0.004	<0.01	<0.01	---	Bal.
6	0.008	0.10	0.07	0.009	0.002	11.54	10.77	1.00	0.05	1.55	0.0020	0.004	<0.01	<0.01	---	Bal.
7	0.008	0.10	0.05	0.009	0.002	11.62	11.05	0.99	0.07	1.58	0.0030	0.003	<0.01	<0.01	---	Bal.
8	0.003	0.07	0.06	0.010	0.001	11.63	10.92	0.75	0.06	1.58	0.0024	0.004	<0.01	<0.01	---	Bal.
9	0.007	0.08	0.07	0.009	0.001	11.49	10.84	0.50	0.06	1.50	0.0023	0.004	<0.01	<0.01	---	Bal.
10	0.012	0.08	0.07	0.010	0.002	11.62	10.84	0.28	0.06	1.50	0.0025	0.002	<0.01	<0.01	---	Bal.
11	0.007	0.10	0.05	0.007	0.001	11.62	10.99	1.49	0.06	1.67	0.0020	0.004	<0.01	<0.01	---	Bal.
12	0.006	0.08	0.05	0.007	0.005	11.58	11.08	0.98	0.05	1.52	0.0017	0.005	0.26	<0.01	---	Bal.
13	0.007	0.08	0.05	0.007	0.005	11.56	10.98	1.00	0.05	1.70	0.0016	0.004	<0.01	<0.01	---	Bal.
14	0.006	0.08	0.05	0.007	0.005	11.55	11.02	1.02	0.05	1.54	0.0018	0.005	<0.01	<0.01	---	Bal.
15	0.008	0.08	0.04	0.007	0.005	11.62	11.03	1.03	0.05	1.54	0.0017	0.004	0.25	<0.01	---	Bal.
16	0.007	0.08	0.04	0.008	0.005	11.68	11.09	1.47	0.05	1.52	0.0017	0.004	0.25	<0.01	---	Bal.
17	0.008	0.08	0.05	0.006	0.003	11.56	10.98	1.00	0.92	1.49	0.0020	0.004	<0.01	<0.01	---	Bal.
18	0.009	0.08	0.04	0.005	0.005	11.60	11.05	1.01	0.92	1.51	0.0024	0.004	<0.01	<0.01	---	Bal.
19	0.011	0.09	0.05	0.008	0.0010	11.63	11.05	1.26	0.06	1.58	0.0014	0.0050	<0.01	<0.01	---	Bal.
20	0.006	0.01	<0.01	<0.005	0.0012	11.60	11.07	1.26	0.02	1.60	0.0013	0.0072	<0.01	<0.01	<0.001	Bal.
21	0.004	0.05	0.04	0.005	0.0008	11.66	10.81	0.75	0.05	1.60	0.0021	0.0056	<0.01	<0.01	<0.001	Bal.
22	0.002	0.05	0.05	<0.005	0.0007	11.62	11.21	1.05	0.05	1.58	0.0021	0.0050	<0.01	<0.01	<0.001	Bal.
23	0.005	0.05	0.05	<0.005	<0.0005	11.65	10.91	0.75	0.06	1.61	0.0020	0.0065	<0.01	<0.01	<0.001	Bal.
24	0.008	0.05	0.04	<0.005	<0.0005	11.64	10.89	0.85	0.05	1.58	0.0019	0.0059	<0.01	<0.01	<0.001	Bal.
25	0.002	0.07	0.03	<0.005	0.0006	11.63	10.99	1.00	0.05	1.56	0.0020	0.0043	<0.01	<0.01	<0.001	Bal.
26	0.009	0.01	0.04	<0.005	<0.0005	11.60	11.00	1.26	0.01	1.63	0.0016	0.0042	<0.01	<0.01	0.006	Bal.
27	0.004	0.01	<0.01	<0.005	0.0005	11.59	11.03	1.26	<0.01	1.60	0.0026	0.0046	<0.01	<0.01	0.002	Bal.
28	0.002	0.05	0.05	<0.005	<0.0005	11.61	11.14	0.90	0.05	1.60	0.0022	0.0038	<0.01	<0.01	0.004	Bal.
29	0.004	0.05	0.04	<0.005	<0.0005	11.55	10.78	0.75	0.05	1.57	0.0018	0.0044	<0.01	<0.01	0.003	Bal.
30	0.007	0.07	0.03	<0.005	<0.0005	11.70	11.08	1.00	0.05	1.53	0.0022	0.0045	<0.01	<0.01	0.002	Bal.
A	0.030	0.02	0.02	0.004	0.006	12.63	8.17	2.13	0.03	0.01	<0.0010	0.006	<0.01	1.10	---	Bal.
B	0.035	0.06	0.06	0.002	0.003	12.61	8.20	2.14	0.06	0.016	<0.0010	0.003	<0.01	1.14	---	Bal.
C	0.007	0.08	0.04	0.008	0.003	11.66	8.61	0.11	2.01	1.10	0.0022	0.005	0.25	<0.01	---	Bal.
D	0.006	0.08	0.05	0.004	0.002	11.58	8.29	0.09	2.14	1.18	0.0028	0.005	0.24	0.022	---	Bal.

1 Also contains 0.002% zirconium

2 Also contains 0.002% zirconium

3 Also contains 0.0009 - 0.0022 weight percent oxygen

4 Also contains 0.0009 - 0.0022 weight percent oxygen

5 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

6 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

7 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

8 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

9 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

10 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

11 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

12 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

13 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

14 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

15 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

16 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

17 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

18 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

19 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

20 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

21 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

22 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

23 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

24 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

25 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

26 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

27 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

28 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

29 Although essentially no cerium was recovered, a mischmetal addition was made during vacuum induction melting

Examples

In order to demonstrate the unique combination of properties provided by the present alloy, Examples 1-24 of the alloy described in co-pending application No. 08/533,159 and Examples 25-30 of the present invention, having the compositions in weight percent shown in Table 1, were prepared. For comparison purposes, Comparative Heats A-D with compositions outside the range of the present invention were also prepared. Their weight percent compositions are also included in Table 1.

Alloys A and B are representative of one of the known precipitation hardening, stainless steel alloys and Alloys C and D are representative of another known precipitation hardening, stainless steel alloy.

Example 1 was prepared as a 17 lb. (7.7 kg) laboratory heat which was vacuum induction melted and cast as a 2.75 inch (6.98 cm) tapered square ingot. The ingot was heated to 1900 °F (1038 °C) and press-forged to a 1.375 inch (3.49 cm) square bar. The bar was finish-forged to a 1.125 inch (2.86 cm) square bar and air-cooled to room temperature. The forged bar was hot rolled at 1850 °F (1010 °C) to a 0.625 inch (1.59 cm) round bar and then air-cooled to room temperature.

Examples 2-4 and 12-18, and Comparative Heats A and C were prepared as 25 lb. (11.3 kg) laboratory heats which were vacuum induction melted under a partial pressure of argon gas and cast as 3.5 inch (8.9 cm) tapered square ingots. The ingots were press-forged from a starting temperature of 1850 °F (1010 °C) to 1.875 inch (4.76 cm) square bars which were then air-cooled to room temperature. The square bars were reheated, press-forged from the temperature of 1850 °F (1010 °C) to 1.25 inch (3.18 cm) square bars, reheated, hot-rolled from the temperature of 1850 °F (1010 °C) to 0.625 inch (1.59 cm) round bars, and then air-cooled to room temperature.

Examples 5, 6, and 8-10 were prepared as 37 lb. (16.8 kg) laboratory heats which were vacuum induction melted under a partial pressure of argon gas and cast as 4 inch (10.2 cm) tapered square ingots. The ingots were
5 press-forged from a starting temperature of 1850 °F (1010 °C) to 2 inch (5.1 cm) square bars and then air-cooled. A length was cut from each 2 inch (5.1 cm) square forged bar and forged from a temperature of 1850 °F (1010 °C) to 1.31 inch (3.33 cm) square bar.
10 The forged bars were hot rolled at 1850°F (1010°C) to 0.625 inch (1.59 cm) round bars and air cooled to room temperature.

Examples 7 and 11, and Comparative Heats B and D were prepared as 125 lb. (56.7 kg) laboratory heats
15 which were vacuum induction melted under a partial pressure of argon gas and cast as 4.5 inch (11.4 cm) tapered square ingots. The ingots were press-forged from a starting temperature of 1850 °F (1010 °C) to 2 inch (5.1 cm) square bars and then air-cooled to room
20 temperature. The bars were reheated and then forged from a temperature of 1850 °F (1010 °C) to 1.31 inch (3.33 cm) square bars. The forged bars were hot rolled at 1850°F (1010°C) to 0.625 inch (1.59 cm) round bars and air cooled to room temperature.

25 Examples 19-30 were prepared as approximately 380 lb. (172 kg) heats which were vacuum induction melted and cast as 6.12 inch (15.6 cm) diameter electrodes. Prior to casting each of the electrodes, mischmetal was added to the respective VIM heats for
30 Examples 25-30. The amount of each addition was selected to result in a desired retained-amount of cerium after refining. The electrodes were vacuum-arc remelted and cast as 8 inch (20.3 cm) diameter ingots. The ingots were heated to 2300°F (1260°C) and
35 homogenized for 4 hours at 2300°F (1260°C). The ingots were furnace cooled to 1850°F (1010°C) and soaked for 10 minutes at 1850°F (1010°C) prior to press forging. The ingots were then press forged to 5 inch (12.7 cm) square

bars as follows. The bottom end of each ingot was pressed to a 5 inch (12.7 cm) square. The forging was then reheated to 1850°F (1010°C) for 10 minutes prior to pressing the top end to a 5 inch (12.7 cm) square. The
5 as-forged bars were cooled in air from the finishing temperature.

The resulting 5 inch (12.7 cm) square bars of Examples 19-24 and 26-29 were cut in half with the billets from the top and bottom ends being separately
10 identified. Each billet from the bottom end was reheated to 1850°F (1010°C), soaked for 2 hours, press forged to 4.5 inch (11.4 cm) by 2.75 inch (6.98 cm) bars and air-cooled to room temperature. Each billet from
15 the top end was reheated to 1850°F (1010°C) and soaked for 2 hours. For Examples 19-24 and 27-29, each top end billet was then press forged to 4.5 inch (11.4 cm) by 1.5 inch (3.8 cm) bars and air-cooled to room
20 temperature. For Example 26, the top end billet was forged to 4.75 inch (12.1 cm) by 2 inch (5.1 cm) bars, reheated to 1850°F (1010°C) for 15 minutes, press forged to 4.5 inch (11.4 cm) by 1.5 inch (3.8 cm) bars and then air-cooled to room temperature.

The 5 inch (12.7 cm) square bars of Examples 25 and 30 were cut in thirds and in half, respectively. The
25 billets were then reheated to 1850°F (1010°C), soaked for 2 hours, press forged to 4.5 inch (11.4 cm) by 1.625 inch (4.13 cm) bars, and then air-cooled to room temperature.

With reference to Examples 1-18 and Heats A-D, the
30 bars of each Example and Comparative Heat were rough turned to produce smooth tensile, stress-corrosion, and notched tensile specimens having the dimensions indicated in Table 2. Each specimen was cylindrical with the center of each specimen being reduced in
35 diameter with a minimum radius connecting the center section to each end section of the specimen. The stress-corrosion specimens were polished to a nominal gage diameter with a 400 grit surface finish.

Table 2

	Specimen Type	Length in./cm	Diameter in./cm	Center Section		Minimum radius in./cm	Gage diameter in. (cm)
				Length in./cm	Diameter in./cm		
5	Smooth tensile	3.5/8.9	0.5/1.27	1.0/2.54	0.25/0.64	0.1875/0.476	---
10	Stress-corrosion	5.5/14.0	0.436/1.11	1.0/2.54	0.25/0.64	0.25/0.64	0.225/0.57
15	Notched tensile ⁽¹⁾	3.75/9.5	0.50/1.27	1.75/4.4	0.375/0.95	0.1875/0.476	---

⁽¹⁾ A notch was provided around the center of each notched tensile specimen. The specimen diameter was 0.252 in. (0.64 cm) at the base of the notch; the notch root radius was 0.0010 inches (0.0025 cm) to produce a stress concentration factor (K_t) of 10.

The test specimens of Examples 1-18 and Heats A-D were heat treated in accordance with Table 3 below. The heat treatment conditions used were selected to provide peak strength.

Table 3

		<u>Solution Treatment</u>	<u>Aging Treatment</u>
25	Exs. 1-18	1800°F(982°C)/1 hour/WQ ^{1,2}	900°F(482°C)/4 hours/AC ³
	Hts. A and B	1700°F(927°C)/1 hour/WQ ⁴	950°F(510°C)/4 hours/AC
	Hts. C and D	1500°F(816°C)/1 hour/WQ	900°F(482°C)/4 hours/AC

¹ WQ= water quenched.

² Cold treated at -100°F (-73°C) for 1 hour then warmed in air.

30 ³ AC= air cooled.

⁴ Cold treated at 33°F (0.6°C) for 1 hour then warmed in air.

The mechanical properties of Examples 1-18 were compared with the properties of Comparative Heats A-D. The properties measured include the 0.2% yield strength (.2% YS), the ultimate tensile strength (UTS), the percent elongation in four diameters (% Elong.), the percent reduction in area (% Red.), and the notch tensile strength (NTS). All of the properties were measured along the longitudinal direction. The results of the measurements are given in Table 4.

Table 4

Ex./Ht. No.	Cr	Ni	Mo	Ti	.2% YS (ksi/Mpa)	UTS (ksi/Mpa)	% Elong.	% Red. in Area	NTS (ksi/Mpa)	NTS/UTS
1	11.54	11.13	1.00	1.61	253.7/1749	264.3/1822	12.0	50.5	309.0/2130*	1.17
2	11.57	11.02	1.00	1.52	244.7/1687	256.2/1766	14.7	53.5	341.2/2352*	1.33
3	11.61	11.03	1.00	1.68	246.8/1702	260.1/1793	12.6	49.4	324.9/2240*	1.25
4	11.60	11.05	1.43	1.52	244.2/1684	256.7/1770	14.4	58.8	352.5/2430*	1.37
5	11.58	10.46	1.00	1.58	248.5/1713*	266.0/1834*	11.5*	49.6*	288.3/1988*	1.08
6	11.54	10.77	1.00	1.55	251.5/1734*	268.3/1850*	11.7*	51.7*	324.9/2240*	1.21
7	11.62	11.05	0.99	1.58	240.5/1658*	261.6/1804*	11.5*	51.1*	344.5/2375*	1.32
8	11.63	10.92	0.75	1.58	250.4/1726*	267.9/1847*	12.4*	54.5*	361.4/2492*	1.35
9	11.49	10.84	0.50	1.58	251.4/1733*	267.9/1847*	11.3*	50.6*	339.3/2333*	1.27
10	11.60	10.84	0.28	1.50	248.4/1713*	264.5/1824*	12.1*	57.0*	347.3/2395*	1.31
11	11.62	10.99	1.49	1.67	227.6/1569*	255.6/1762*	11.6*	47.9*	332.8/2295*	1.30
12	11.58	11.08	0.98	1.52	250.7/1728	262.4/1809	12.2	52.4	312.2/2153*	1.19
13	11.56	10.98	1.00	1.70	255.8/1764	270.2/1863	13.2	50.2	281.6/1942*	1.04
14	11.55	11.02	1.02	1.54	248.7/1714	262.9/1813	13.9	50.7	262.2/1808*	1.00
15	11.62	11.03	1.03	1.54	247.8/1708	262.4/1809	12.4	48.3	289.3/1995*	1.10
16	11.68	11.09	1.47	1.52	238.3/1643	251.2/1732	15.9	56.0	318.6/2197*	1.27
17	11.56	10.98	1.00	1.49	239.2/1649	254.6/1755	12.7	39.6	289.0/1993*	1.14
18	11.60	11.05	1.01	1.51	235.3/1622	250.0/1724	11.8	42.4	311.9/2150*	1.25
A	12.63	8.17	2.13	0.01	210.1/1449	224.4/1547	14.4	59.4	346.9/2392*	1.54
B	12.61	8.20	2.14	0.016	209.2/1442	230.1/1586	15.9	65.4	349.8/2412	1.52
C	11.66	8.61	0.11	1.10	250.5/1727	254.3/1753	12.2	52.0	319.6/2204*	1.26
D	11.58	8.29	0.09	1.18	251.0/1731	259.3/1788	10.7	46.7	329.7/2273	1.27

* The value reported is an average of two measurements.

The data in Table 4 show that Examples 1-18 of the present invention provide superior yield and tensile strength compared to Heats A and B, while providing acceptable levels of notch toughness, as indicated by the NTS/UTS ratio, and ductility. Thus, it is seen that Examples 1-18 provide a superior combination of strength and ductility relative to Heats A and B.

Moreover, the data in Table 4 also show that Examples 1-18 of the present invention provide tensile strength that is at least as good as to significantly better than Heats C and D, while providing acceptable yield strength and ductility, as well as an acceptable level of notch toughness as indicated by the NTS/UTS ratio.

The stress-corrosion cracking resistance properties of Examples 7-11 in a chloride-containing medium were compared to those of Comparative Heats B and D via slow-strain-rate testing. For the stress-corrosion cracking test, the specimens of Examples 7-11 were solution treated similarly to the tensile specimens and then over-aged at a temperature selected to provide a high level of strength. The specimens of Comparative Heats B and D were solution treated similarly to their respective tensile specimens, but over-aged at a temperature selected to provide the level of stress-corrosion cracking resistance typically specified in the aircraft industry. More specifically, Examples 7-11 were age hardened at 1000°F (538°C) for 4 hours and then air-cooled and Comparative Heats B and D were age hardened at 1050°F (566 °C) for 4 hours and then air-cooled.

The resistance to stress-corrosion cracking was tested by subjecting sets of the specimens of each example/heat to a tensile stress by means of a constant extension rate of 4×10^{-6} inches/sec (1×10^{-5} cm/sec). Tests were conducted in each of four different media: (1) a boiling solution of 10.0% NaCl acidified to pH 1.5 with H_3PO_4 ; (2) a boiling solution of 3.5% NaCl at its

natural pH (4.9 - 5.9); (3) a boiling solution of 3.5% NaCl acidified to pH 1.5 with H_3PO_4 ; and (4) air at 77 °F (25 °C). The tests conducted in air were used as a reference against which the results obtained in the chloride-containing media could be compared.

The results of the stress-corrosion testing are given in Table 5 including the time-to-fracture of the test specimen (Total Test Time) in hours, the percent elongation (% Elong.), and the reduction in cross-sectional area (% Red. in Area).

Table 5

Ex./Ht. No.	Environment	Total Test Time (hrs)	% Elong.	% Red. in Area
5	7 Boiling 10.0% NaCl at pH 1.5	8.5	4.9	21.5
	"	9.4	5.4	25.0
	Boiling 3.5% NaCl at pH 1.5	13.5	11.3	53.7
	"	13.6	11.1	58.6
	"	12.6	11.5	53.9
10	Boiling 3.5% NaCl at pH 5.8	14.4	12.0	62.0
	"	13.8	11.7	60.2
	Air at 77°F (25°C)	14.4	12.6	60.4
	"	12.6	10.6	58.6
	"	14.2	12.8	56.1
15	8 Boiling 10.0% NaCl at pH 1.5	8.2	5.4	23.8
	"	8.3	5.3	21.4
	Boiling 3.5% NaCl at pH 1.5	13.0	11.0	54.4
	"	13.3	11.0	53.4
	Boiling 3.5% NaCl at pH 5.9	13.9	13.8	64.8
20	"	14.1	13.8	64.1
	"	14.0	13.4	62.4
	Air at 77°F (25°C)	14.6	14.3	63.7
	"	14.0	13.6	63.2
25	9 Boiling 10.0% NaCl at pH 1.5	10.0	6.6	20.6
	"	10.3	6.2	20.7
	Boiling 3.5% NaCl at pH 1.5	12.6	10.6	50.1
	"	12.8	12.0	49.5
	Boiling 3.5% NaCl at pH 4.9	13.6	12.2	55.8
30	"	13.6	12.0	54.4
	Air at 77°F (25°C)	13.8	12.6	59.6
	"	14.0	12.8	58.5
	10 Boiling 10.0% NaCl at pH 1.5	9.6	7.0	27.9
	"	10.4	7.7	17.9
	Boiling 3.5% NaCl at pH 1.5	13.7	11.8	58.1
35	"	13.8	11.5	54.0
	Boiling 3.5% NaCl at pH 5.9	13.5	13.3	61.8
	"	14.3	14.6	61.7
	"	14.0	11.9	52.8
	Air at 77°F (25°C)	14.4	13.1	63.8
40	"	14.4	12.7	63.9
	11 Boiling 10.0% NaCl at pH 1.5	9.5	6.5	20.8
	"	9.5	5.0	22.2
	"	11.3	7.2	22.9
	Boiling 3.5% NaCl at pH 1.5	13.5	10.8	58.6
45	"	13.9	11.0	56.5
	"	13.0	11.6	53.2
	Boiling 3.5% NaCl at pH 5.8	14.6	12.3	62.8
	"	14.1	12.7	61.6
	Air at 77°F (25°C)	14.4	12.7	61.5
50	"	13.4	11.5	58.5
	"	13.6	11.3	53.8
	B Boiling 10.0% NaCl at pH 1.5	14.9	14.5	51.7
	"	15.2	16.6	65.2
	"	13.7	12.9	59.8
55	Boiling 3.5% NaCl at pH 1.5	14.2	13.3	69.9
	"	13.5	14.0	69.9
	"	13.8	14.5	68.4
	Boiling 3.5% NaCl at pH 5.8	13.4	13.9	66.1
	"	13.6	13.3	67.6
60	Air at 77°F (25°C)	14.1	15.1	69.9
	"	15.1	15.7	69.7
	"	15.4	15.4	69.3
	D Boiling 10.0% NaCl at pH 1.5	7.4	3.7	6.9
	"	9.6	8.3	15.6
65	"	10.2	10.0	19.2
	Boiling 3.5% NaCl at pH 1.5	13.4	11.3	49.6
	"	13.2	10.1	46.1
	"	12.8	10.7	44.5
	Boiling 3.5% NaCl at pH 5.8	13.4	11.5	51.3
70	"	13.4	11.9	52.0
	Air at 77°F (25°C)	14.1	15.2	56.0
	"	15.1	14.4	54.4
	"	15.8	15.4	59.6
75	These measurements represent the reference values for the boiling 10.0% NaCl test conditions only.			

The relative stress-corrosion cracking resistance of the tested alloys can be better understood by reference to a ratio of the measured parameter in the corrosive medium to the measured parameter in the reference medium. Table 6 summarizes the data of Table 5 by

presenting the data in a ratio format for ease of comparison. The values in the column labeled "TC/TR" are the ratios of the average time-to-fracture under the corrosive condition to the average time-to-fracture under the reference condition. The values in the column labeled "EC/ER" are the ratios of the average % elongation under the indicated corrosive condition to the average % elongation under the reference condition. Likewise, the values in the column labeled "RC/RR" are the ratios of the average % reduction in area under the indicated corrosive condition to the average % reduction in area under the reference condition.

Table 6

15

Ex./Ht.
No. TC/TR⁽¹⁾ EC/ER⁽²⁾ RC/RR⁽³⁾

20

(Boiling 10.0% NaCl at pH 1.5)

7	.67	.44	.41
8	.58	.38	.36
9	.73	.50	.35
10	.69	.57	.36
11	.75	.55	.39
B	.96	.94	.85
D	.59	.49	.24

25

(Boiling 3.5% NaCl at pH 1.5)

7	.92	.90	.92
8	.92	.79	.85
9	.91	.89	.84
10	.95	.90	.88
11	.94	.88	.91
B	.98	.92	.99
D	.93	.70	.83

30

35

(Boiling 3.5% NaCl at pH 4.9-5.9)

7	.98	.94	1.0
8	.98	.98	1.0
9	.98	.95	.93
10	.97	1.0	.92
11	1.0	.98	1.0
B	.96	.90	.96
D	.95	.77	.92

40

45

⁽¹⁾ TC/TR = Average time-to-fracture under corrosive conditions divided by average time-to-fracture under reference conditions.

50

⁽²⁾ EC/ER = Average elongation under corrosive conditions divided by average elongation under reference conditions.

55

⁽³⁾ RC/RR = Average reduction in area under corrosive conditions divided by average reduction in area under reference conditions.

The mechanical properties of Examples 7-11 and Heats B and D were also determined and are presented in Table 7 including the 0.2% offset yield strength (.2% YS) and the ultimate tensile strength (UTS) in ksi (MPa), the percent elongation in four diameters (% Elong.), the reduction in area (% Red. in Area), and the notch tensile strength (NTS) in ksi (MPa).

Table 7

Ex./Ht. No.	Condition	.2% YS (ksi/MPa)	UTS (ksi/MPa)	% Elong.	% Red. in Area	NTS (ksi/MPa)
7	H1000	216.8/1495	230.5/1589	15.0	62.5	344.6/2376
8	H1000	223.0/1538	233.6/1611	14.5	64.0	353.0/2434
9	H1000	223.4/1540	234.8/1619	14.8	64.3	349.6/2410
10	H1000	219.3/1512	230.0/1586	14.4	65.0	348.6/2404
11	H1000	210.5/1451	230.9/1592	15.0	63.0	344.2/2373
B	H1050	184.1/1269	190.8/1316	17.9	72.3	303.4/2092
D	H1050	182.9/1261	196.9/1358	17.6	62.1	296.3/2043

When considered together, the data presented in Tables 6 and 7 demonstrate the unique combination of strength and stress corrosion cracking resistance provided by the alloy according to the present invention, as represented by Examples 7-11. More particularly, the data in Tables 6 and 7 show that Examples 7-11 are capable of providing significantly higher strength than comparative Heats B and D, while providing a level of stress corrosion cracking resistance that is comparable to those alloys. Additional specimens of Examples 7 and 11 were age hardened at 1050°F (538°C) for 4 hours and then air-cooled. Those specimens provided room temperature ultimate tensile strengths of 214.3 ksi and 213.1 ksi, respectively, which are still significantly better than the strength provided by Heats B and D when similarly aged. Although not tested, it would be expected that the stress corrosion cracking resistance of Examples 7 and 11 would be at least the same or better when aged at the higher temperature. In addition, it should be noted that the boiling 10.0% NaCl conditions are more severe than recognized standards for the aircraft industry.

With reference to Examples 19-30, the bars of each example were rough turned to produce smooth tensile and notched tensile specimens having the dimensions indicated in Table 2. Each specimen was cylindrical with the center of each specimen being reduced in diameter and a minimum radius connecting the center section to each end section of the specimen. In addition, CVN test specimens (ASTM E 23-96) and compact tension blocks for fracture toughness testing (ASTM E399) were machined from the annealed bar. All of the test specimens were solution treated at 1800°F (982°C) for 1 hour then water quenched, cold treated at -100°F (-73°C) for either 1 or 8 hours then warmed in air, and aged at either 900°F (482°C) or 1000°F (538°C) for 4 hours then air cooled.

The mechanical properties measured include the 0.2% yield strength (.2% YS), the ultimate tensile strength (UTS), the percent elongation in four diameters (% Elong.), the percent reduction in area (% Red.), the notch tensile strength (NTS), the room-temperature Charpy V-notch impact strength (CVN), and the room-temperature fracture toughness (K_{Ic}). The results of the measurements are given in Tables 8-11.

Table 8

Ex./Ht. No.	Bar Size (in./cm)	Orientation	24 YS (ksi/MPa)	UTS (ksi/MPa)	Elong. in Area	Red. in Area	NTS (ksi/MPa)	NTS/UTS (ft-lb/lb)	CVN (ft-lb/lb)	K _{1C} or K _{IC} (ksi√in/MPa√m)
26	4.5x2.75/11x7.0	Longitudinal	231.3/1595	249.0/1717	13.8	55.7	328.6/2266	1.32	10/141	72.6/79.8
		Transverse	227.1/1566	245.3/1691	10.9	40.8	318.5/2196	1.30	9/121	68.7/75.5
	4.5x1.5/11x3.8	Longitudinal	236.4/1630	254.2/1753	13.3	54.6	342.3/2360	1.35	12/161	74.6/82.0
		Transverse	230.3/1588	255.4/1761	12.3	51.9	320.1/2207	1.25	12/161	74.9/82.3
27	4.5x2.75/11x7.0	Longitudinal	224.0/1544	246.4/1699	14.8	59.0	349.9/2412	1.42	21/281	90.9/99.9
		Transverse	211.4/1458	239.2/1649	14.0	50.9	343.9/2371	1.44	14/191	79.9/87.8
	4.5x1.5/11x3.8	Longitudinal	221.2/1525	242.9/1675	14.5	61.1	348.4/2402	1.43	19/261	95.5/105
		Transverse	213.7/1473	245.8/1695	13.5	51.1*	348.1/2400	1.42	18/241	94.0/92.3
28	4.5x2.75/11x7.0	Longitudinal	234.8/1619	253.6/1748	12.5	54.9	332.0/2289	1.31	11/151	69.4/76.2
		Transverse	232.7/1604	252.8/1743	12.1	51.7	335.3/2312	1.33	10/141	71.9/79.0
	4.5x1.5/11x3.8	Longitudinal	231.1/1593	252.0/1738	12.6	54.4	328.5/2265	1.30	11/151	78.8/86.6
		Transverse	228.8/1578	252.6/1748	12.4	53.6	330.2/2277	1.30	9/121	73.7/81.0
19	4.5x2.75/11x7.0	Longitudinal	223.6/1542	244.3/1684	14.3	55.9	341.3/2353	1.40	15/201	89.9/98.8
		Transverse	224.0/1544	243.8/1681	10.8	43.0	313.3/2160	1.29	8/111	71.2/78.2
	4.5x1.5/11x3.8	Longitudinal	222.7/1536	243.2/1677	15.0	60.0	343.3/2367	1.41	19/261	94.0/103
		Transverse	215.7/1487	241.0/1662	11.6	43.5	325.4/2244	1.35	11/151	82.1/90.2
20	4.5x2.75/11x7.0	Longitudinal	229.8/1584	247.8/1708	13.7	57.5	343.8/2370	1.39	9/121	74.0/81.3
		Transverse	229.2/1580	249.2/1718	12.6	49.8	324.9/2240	1.30	10/141	70.3/77.2
	4.5x1.5/11x3.8	Longitudinal	225.9/1558	244.5/1686	14.3	58.2	339.2/2339	1.39	11/151	82.6/90.8
		Transverse	229.3/1581	249.1/1718	12.1	48.7	334.2/2304	1.34	11/151	81.4/89.4
21	4.5x2.75/11x7.0	Longitudinal	242.6/1673	260.4/1795	11.8	53.6	334.1/2304	1.34	5/71	48.5/53.3
		Transverse	245.2/1691	263.5/1817	10.3	43.7	318.8/2159	1.02	6/81	47.0/51.6
	4.5x1.5/11x3.8	Longitudinal	240.8/1660	258.9/1785	12.2	51.3	325.8/2182	1.02	5/71	55.8/61.3
		Transverse	237.0/1676	262.4/1809	10.8	47.4	325.5/2182	0.90	5/71	53.3/58.6
22	4.5x2.75/11x7.0	Longitudinal	227.0/1565	246.5/1700	13.4	56.0	332.7/2290	1.35	10/141	76.4/84.0
		Transverse	226.8/1564	248.8/1715	12.3	50.4	322.7/2225	1.30	10/141	74.0/81.3
	4.5x1.5/11x3.8	Longitudinal	226.2/1560	246.3/1698	13.3	55.7	329.3/2270	1.34	12/161	85.6/94.1
		Transverse	221.0/1538	247.4/1706	11.6	47.9	318.9/2199	1.29	11/151	75.4/82.8

The test specimens were solution treated at 1800°F (982°C) for 1 hour then water quenched, cold treated at -100°F (-73°C) for 1 hour then warmed in air, and aged at 900°F (482°C) for 4 hours then air cooled. The values reported are an average of two measurements, except for the values indicated with a "*" which are from a single measurement and the values indicated with a "†" which are an average of three measurements.

Table 2

Ex./Ht. No.	Bar Size (in./cm)	Orientation	2% YS (ksi/MPa)	UTS (ksi/MPa)	Elong. in Area	% Red. in Area	NTS (ksi/MPa)	NTS/UTS (ft-lb/J)	CVN (ft-lb/J)	K _{1C} or K _{IC} (ksi√in/MPa√m)
26	4.5x2.75/11x7.0	Longitudinal	209.1/1442	225.1/1552	15.2	63.9	340.3/2346	1.51	29/391	108.9/119.7
		Transverse	210.0/1448	225.2/1553	13.4	54.5	342.8/2395	1.48	19/261	98.2/108
		Longitudinal	212.1/1456	227.9/1571	15.1	63.0	342.8/2395	1.50	28/381	113.6/124.8
27	4.5x1.5/11x3.8	Longitudinal	212.1/1456	225.0/1551	13.3	56.2	343.9/2371	1.56	22/30	97.0/106
		Transverse	204.8/1412	220.0/1517	17.0	67.8	343.9/2371	1.56	47/641	109.6/120.4
		Longitudinal	201.7/1386	220.1/1518	15.1	62.2	343.9/2371	1.57	30/411	103.2/113.4
28	4.5x2.75/11x7.0	Longitudinal	205.7/1418	219.4/1513	17.4	68.2	343.9/2371	1.57	50/681	115.8/127.2
		Transverse	206.3/1426	221.3/1526	14.3	57.7	343.9/2371	1.50	34/46	106.3/116.8
		Longitudinal	209.9/1447	224.8/1550	15.2	65.0	340.0/2344	1.51	39/531	97.9/108.6
29	4.5x1.5/11x3.8	Longitudinal	210.5/1451	225.7/1556	14.5	62.2	338.8/2336	1.50	31/421	111.7/122.7
		Transverse	210.6/1452	224.7/1549	15.4	66.0	332.9/2295	1.48	39/531	111.7/122.7
		Longitudinal	206.3/1422	221.8/1529	14.1	61.6	332.9/2295	1.47	31/421	105.6/116.0
30	4.5x2.75/11x7.0	Longitudinal	201.2/1387	217.0/1496	16.1	64.5	335.5/2313	1.55	31/421	112.4/123.5
		Transverse	201.3/1388	219.5/1513	12.7	48.9	320.0/2206	1.46	14/191	113.1/124.3
		Longitudinal	197.1/1359	213.3/1471	16.9	66.3	328.9/2268	1.54	40/541	101.6/111.6
31	4.5x1.5/11x3.8	Longitudinal	196.9/1358	211.4/1458	14.9	53.2	300.4/2071	1.42	17/23	93.7/103
		Transverse	209.3/1443	223.5/1541	16.5	67.0	347.8/2398	1.56	33/451	105.4/115.8
		Longitudinal	211.0/1455	225.6/1556	12.7	49.9	337.9/2330	1.50	22/301	99.7/110
32	4.5x2.75/11x7.0	Longitudinal	207.4/1429	219.5/1513	16.2	66.6	343.0/2365	1.56	36/491	111.3/122.3
		Transverse	207.2/1429	221.8/1529	14.3	59.4	343.0/2365	1.53	23/31	103.6/113.8
		Longitudinal	216.4/1492*	229.4/1592	14.8	65.6	342.0/2358	1.49	20/271	89.3/98.1
33	4.5x1.5/11x3.8	Longitudinal	217.6/1511	231.6/1597	13.2	59.4	342.1/2366	1.48	17/231	86.0/94.5
		Transverse	217.6/1511	230.7/1591	14.8	64.4	340.6/2348	1.48	17/231	100.0/109.9
		Longitudinal	218.5/1506	230.7/1591	12.0	54.8	329.8/2274	1.48	17/231	92.4/102
34	4.5x2.75/11x7.0	Longitudinal	203.8/1405	219.6/1514	15.5	65.5	325.6/2245	1.50	42/571	95.6/105
		Transverse	202.7/1398	219.2/1511	13.6	55.4	325.6/2245	1.49	28/381	97.7/107
		Longitudinal	202.6/1397	219.4/1506	16.0	66.1	325.6/2245	1.49	44/601	110.0/120.9
35	4.5x1.5/11x3.8	Longitudinal	202.2/1394	219.6/1514	13.7	57.1	327.0/2255	1.49	25/34	99.8/110
		Transverse	202.2/1394	219.6/1514	13.7	57.1	327.0/2255	1.49	25/34	99.8/110

The test specimens were solution treated at 1800°F (982°C) for 1 hour then water quenched, cold treated at -100°F (-73°C) for 1 hour then warmed in air, and aged at 1000°F (538°C) for 4 hours then air cooled. The values reported are an average of two measurements, except for the values indicated with a "*" which are from a single measurement and the values indicated with a "1" which are an average of three measurements.

Table 10

Ex./Rt. No.	Bar Size (in./cm)	Orientation	2 $\frac{1}{2}$ YS (ksi/MPa)	UTS (ksi/MPa)	% Elong.	% Red in Area	NTS (ksi/MPa)	NTS/UTS (ft.-lb./J)	CVN (ft.-lb./J)	K _{IC} or K _{IC} (ksi√in/MPa√m)
27	4.5x2.75/11x7.0	Longitudinal	234.8/1619	259.8/1791	13.2	58.2	352.4/2430*	1.36	---	---
28	4.5x2.75/11x7.0	Longitudinal	233.8/1612	254.7/1756	12.8	56.3	336.5/2320	1.32	---	---
		Longitudinal	233.0/1648	258.8/1784	12.8	56.3	336.5/2320	1.32	---	---
		Transverse	234.1/1614	256.3/1767	12.1	51.3	320.8/2212	1.25	---	70.7/77.7
		Longitudinal	238.4/1644	258.0/1779	12.8	55.8	335.5/2313	1.30	---	---
29	4.5x1.5/11x3.8	Longitudinal	241.3/1664	260.2/1794	12.6	56.0	297.2/2049	1.14	6/8	56.5/62.1
		Longitudinal	246.5/1700	264.8/1826	10.3	45.3	305.3/2105	1.15	6/8	55.5/61.0
		Transverse	239.8/1653	258.9/1785	12.9	56.7	331.0/2282	1.28	8/11	62.3/69.1
		Longitudinal	238.5/1644	257.4/1775	11.6	49.5	314.5/2168	1.22	6/8	62.8/69.0
		Transverse	236.2/1628	255.8/1764	12.3	58.6	358.8/2474	1.40	---	81.2/89.2
30	4.5x1.62/11x4.11	Longitudinal	233.3/1609	256.5/1769	12.2	50.6	359.0/2475	1.40	---	71.6/78.7
		Transverse	227.6/1569	256.5/1768	13.0	57.9	346.2/2387	1.35	---	---
19	4.5x2.75/11x7.0	Longitudinal	236.6/1631	257.4/1775	12.9	56.8	346.1/2386	1.34	---	---
20	4.5x2.75/11x7.0	Longitudinal	242.9/1675	263.1/1814	12.1	52.5	344.1/2372	1.35	---	---
21	4.5x2.75/11x7.0	Longitudinal	231.7/1598	254.1/1752	13.6	58.8	281.3/1940	1.09	5/7	58.5/64.3
22	4.5x2.75/11x7.0	Longitudinal	238.8/1646	258.9/1785	12.6	55.0	281.3/1940	1.14	6/8	56.0/61.5
23	4.5x2.75/11x7.0	Longitudinal	240.4/1658	259.2/1787	10.7	43.9	294.2/2028	1.24	7/9	66.7/73.3
		Transverse	235.1/1621	254.5/1755	12.7	54.6	316.0/2179	1.24	7/9	60.1/66.0
		Longitudinal	236.4/1630	256.5/1768	11.3	48.4	280.5/1937	1.10	7/9	63.3/70.0
		Transverse	237.7/1639	257.3/1774	12.9	56.2	339.9/2344	1.32	7/9	58.7/64.5
24	4.5x2.75/11x7.0	Longitudinal	240.0/1655	260.8/1798	9.5	39.1	307.4/2120	1.38	8/11	71.9/79.0
		Transverse	233.9/1613	253.4/1747	13.7	59.5	336.4/2319	1.33	9/12	66.6/73.2
		Longitudinal	233.8/1612	254.3/1753	11.4	47.7	310.5/2141	1.22	8/11	69.0/75.8
		Transverse	238.6/1645	257.4/1775	13.2	58.2	332.2/2290	1.29	---	---
25	4.5x1.62/11x4.11	Longitudinal	232.9/1606	258.3/1781	13.0	51.4	325.0/2241	1.26	---	57.2/73.8

The test specimens were solution treated at 1800°F (982°C) for 1 hour then water quenched, cold treated at -100°F (-73°C) for 8 hours then warmed in air, and aged at 900°F (482°C) for 4 hours then air cooled. The value reported is an average of two measurements, except for the values indicated with a "*" which are from a single measurement and the values indicated with a "†" which are an average of three measurements.

Table 11

Ex./Ht. No.	Bar Size (in./cm)	Orientation	2% YS (ksi/MPa)	UTS (ksi/MPa)	% Elong.	% Red. in Area	NTS (ksi/MPa)	NTS/UTS	CVN (ft-lb/J)	K _{IC} or K _{IC} (ksi√in/MPa√m)
28	4.5x2.75/11x7.0	Longitudinal	214.0/1476	228.9/1578	15.2	65.9	335.2/2311*	1.46	35/47	---
		Transverse	218.2/1504	232.1/1600	15.1	66.2	335.2/2311	1.46	36/49	---
		Longitudinal	212.5/1465	227.0/1565	14.6	62.2	346.3/2388*	1.53	---	108.0/118.7
30	4.5x1.5/11x3.8	Longitudinal	213.8/1474	227.9/1571	14.9	64.1	353.4/2437	1.53	---	---
		Longitudinal	216.2/1491	230.3/1588	15.7	66.0	350.0/2433	1.53	---	120.8/132.7
		Transverse	210.3/1450	225.5/1562	14.3*	58.6*	344.2/2373	1.53	---	108.2/118.9
23	4.5x2.75/11x7.0	Longitudinal	218.2/1491	228.7/1577	14.9	65.1	344.2/2373	1.53	27/37	102.3/112.4
		Transverse	217.9/1502	231.0/1593	12.6	53.5	336.4/2319	1.46	22/30	91.1/100.1
		Longitudinal	214.6/1480	227.6/1569	14.9	65.7	347.7/2397	1.53	28/38	107.5/118.1
24	4.5x1.5/11x3.8	Longitudinal	212.5/1465	226.0/1558	12.8	56.7	339.1/2338	1.51	21/28	97.8/107.5
		Transverse	218.2/1491	227.3/1577*	14.9*	64.6*	344.2/2373	1.51	32/43	102.5/112.6
		Longitudinal	215.4/1485	228.7/1579	12.8	53.3	334.8/2308	1.46	23/31	96.2/105.7
25	4.5x2.75/11x7.0	Longitudinal	210.9/1454	224.7/1549	15.5	66.4	347.5/2396	1.55	30/41	109.4/120.2
		Transverse	218.2/1504	232.0/1600	15.1	64.4	350.3/2415	1.51	21/28	95.8/105.2
		Longitudinal	215.8/1488	228.5/1576	14.7	64.3	342.8/2361	1.50	28/38	102.5/112.6
29	4.5x1.5/11x3.8	Longitudinal	221.0/1534*	232.8/1605*	12.0*	52.9*	342.4/2361	1.47	26/35	100.3/110.2
		Transverse	217.0/1496	229.4/1592	14.9	65.4	347.9/2399	1.52	28/38	107.8/118.4
		Longitudinal	215.7/1487	228.5/1576	13.4	59.5	338.9/2337	1.48	24/32	104.8/115.2

The test specimens were solution treated at 1800°F (982°C) for 1 hour then water quenched, cold treated at -100°F (-73°C) for 8 hours, then warmed in air, and aged at 1000°F (538°C) for 4 hours then air cooled. The values reported are an average of two measurements, except for the values indicated with a "*" which are from a single measurement and the values indicated with a "1" which are an average of three measurements.

The terms and expressions that have been employed herein are used as terms of description and not of limitation. There is no intention in the use of such terms and expressions to exclude any equivalents of the
5 features described or any portions thereof. It is recognized, however, that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A precipitation hardenable, martensitic stainless steel alloy having a unique combination of stress-corrosion cracking resistance, strength, and notch toughness consisting essentially of, in weight percent, about

	C	0.03 max
	Mn	1.0 max
	Si	0.75 max
10	P	0.040 max
	S	0.020 max
	Cr	10 - 13
	Ni	10.5 - 11.6
	Ti	1.5 - 1.8
15	Mo	0.25 - 1.5
	Cu	0.95 max
	Al	0.25 max
	Nb	0.3 max
	B	0.010 max
20	N	0.030 max
	Ce	0.001 - 0.025

the balance essentially iron.

2. The alloy recited in Claim 1 which contains no more than about 0.015 weight percent cerium.
3. The alloy recited in Claim 1 which contains no more than about 0.010 weight percent cerium.
- 30 4. The alloy recited in Claim 1 which contains at least about 0.002 weight percent cerium.
5. The alloy recited in Claim 1 which contains no more than about 0.75 weight percent copper.
- 35 6. The alloy recited in Claim 5 which contains no more than about 0.015 weight percent cerium.
7. The alloy recited in Claim 5 which contains no more than about 0.010 weight percent cerium.
- 40

8. The alloy recited in Claim 5 which contains at least about 0.002 weight percent cerium.

9. A method of preparing a precipitation hardenable, martensitic stainless steel alloy having a unique combination of stress-corrosion cracking resistance, strength, and notch toughness, said alloy consisting essentially of the following elements in the following approximate weight percents:

10	C	0.03 max
	Mn	1.0 max
	Si	0.75 max
	P	0.040 max
	S	0.020 max
15	Cr	10 - 13
	Ni	10.5 - 11.6
	Ti	1.5 - 1.8
	Mo	0.25 - 1.5
	Cu	0.95 max
20	Al	0.25 max
	Nb	0.3 max
	B	0.010 max
	N	0.030 max

and the balance essentially iron, said method comprising the steps of:

melting charge materials containing said elements in proportions sufficient to provide said weight percent amounts; and

adding cerium to the alloy during the melting thereof, the ratio of the amount of cerium added to the amount of sulfur present in the alloy being at least about 1:1.

10. The method recited in Claim 9 wherein the step of adding cerium to the alloy comprises the step of adding cerium to the alloy in an amount such that the ratio of the amount of cerium added to the amount of sulfur present in the alloy is at least about 2:1.

11. The method recited in Claim 10 wherein the step of adding cerium to the alloy comprises the step of adding cerium to the alloy in an amount such that the ratio of

the amount of cerium added to the amount of sulfur present in the alloy is at least about 3:1.

12. The method recited in Claim 9 wherein the step of adding cerium to the alloy comprises the step of adding cerium to the alloy in an amount such that the ratio of the amount of cerium added to the amount of sulfur present in the alloy is not more than about 15:1.

13. The method recited in Claim 12 wherein the step of adding cerium to the alloy comprises the step of adding cerium to the alloy in an amount such that the ratio of the amount of cerium added to the amount of sulfur present in the alloy is not more than about 12:1.

14. A precipitation hardenable, martensitic stainless steel alloy product having a unique combination of stress-corrosion cracking resistance, strength, and notch toughness, said alloy consisting essentially of, in weight percent, about

	C	0.03 max
	Mn	1.0 max
	Si	0.75 max
	P	0.040 max
	S	0.020 max
25	Cr	10 - 13
	Ni	10.5 - 11.6
	Ti	1.5 - 1.8
	Mo	0.25 - 1.5
30	Cu	0.95 max
	Al	0.25 max
	Nb	0.3 max
	B	0.010 max
	N	0.030 max
35	Ce	up to 0.025

and the balance essentially iron, said alloy product being prepared by:

melting charge materials containing C, Mn, Si, P, S, Cr, Ni, Ti, Mo, Cu, Al, Nb, B, N, and Fe in proportions sufficient to provide said weight percent amounts; and adding cerium to the alloy during the melting thereof, the ratio of the amount of cerium added to the

amount of sulfur present in the alloy being at least about 1:1.

15. The product recited in Claim 14 which is prepared
5 by adding cerium to the alloy in an amount such that the ratio of the amount of cerium added to the amount of sulfur present in the alloy is at least about 2:1.

16. The product recited in Claim 15 which prepared by
10 adding cerium to the alloy in an amount such that the ratio of the amount of cerium added to the amount of sulfur present in the alloy is at least about 3:1.

17. The product recited in Claim 14 which is prepared
15 by adding cerium to the alloy in an amount such that the ratio of the amount of cerium added to the amount of sulfur present in the alloy is not more than about 15:1.

18. The product recited in Claim 17 which is prepared
20 by adding cerium to the alloy in an amount such that the ratio of the amount of cerium added to the amount of sulfur present in the alloy is not more than about 12:1.

INTERNATIONAL SEARCH REPORT

Internat	Application No
PCT/US 98/15839	

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C22C38/44 C22C38/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 12073 A (CRS HOLDINGS INC) 3 April 1997	9-19
Y	see page 3	1-8
Y	WO 96 03532 A (NIPPON STEEL CORP ;ASAHI HITOSHI (JP); HARA TAKUYA (JP); KAWAKAMI) 8 February 1996 see page 10, paragraph 1	1-19
Y	EP 0 565 117 A (SUMITOMO METAL IND) 13 October 1993 see page 5, paragraph 47-49	1-19
A	DE 27 44 047 A (THYSSEN EDELSTAHLWERKE AG) 19 April 1979	1-19
A	EP 0 604 062 A (ETHICON INC) 29 June 1994	1-19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

22 September 1998

20/10/1998

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Badcock, G

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/15839

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9712073 A	03-04-1997	US 5681528 A EP 0859869 A	28-10-1997 26-08-1998
WO 9603532 A	08-02-1996	CN 1159213 A EP 0771366 A JP 10503809 T	10-09-1997 07-05-1997 07-04-1998
EP 0565117 A	13-10-1993	JP 5287455 A DE 69312367 D DE 69312367 T US 5383983 A	02-11-1993 28-08-1997 26-02-1998 24-01-1995
DE 2744047 A	19-04-1979	NONE	
EP 0604062 A	29-06-1994	AT 165629 T AU 664928 B AU 5203893 A BR 9304977 A CA 2110928 A DE 69318274 D ES 2115028 T GR 93100464 A JP 7070703 A US 5651843 A	15-05-1998 07-12-1995 23-06-1994 28-06-1994 10-06-1994 04-06-1998 16-06-1998 31-08-1994 14-03-1995 29-07-1997